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Differences in Fundamental Reaction Mechanisms between High and Low LET in Recent Advancements and Applications of Ionizing Radiation

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Abstract

Differences between the mechanisms of energy deposition by high-LET radiation, consisting of neutrons, protons, alpha particles, and heavy ions on one hand, and low-LET radiation, exemplified by electron beam and gamma radiation on the other, are utilized in the selection of types of radiation used for specific applications. Thus, high-LET radiation is used for modification of carbon nanotubes, for ion track grafting, and the synthesis of membranes and nanowires, as well as for characterization of materials by means of neutron scattering. Recent applications of low-LET irradiation include minimization of radiolytic degradation upon sterilization of ultrahigh molecular weight polyethylene (UHMWPE), radiolytic synthesis of nanogels for drug delivery systems, grafting of polymers in the synthesis of adsorbrnts for uranium from seawater, and reductive remediation of PCBs.

Key Words

High LET, Low LET

Introduction

In recent years, radiation engineering (i.e., the use of ionizing radiation in the advanced manufacturing and processing industries, reliability and risk assessment, manufacturing of nano-composites and nano-gels, electron beam-based manufacturing of thin film polymer materials, electron lithography, environmental remediation engineering, radiation therapy, corrosion inhibition in nuclear power plants, and sterilization of medical equipment) has become a vital field in modern technology.[1] Within this area, the current research interests throughout the globe are concentrated on several topics of major importance.

Since its dawn, nanotechnology has been fundamentally connected to nuclear applications and, in particular, high-energy ionizing radiation. One successful example is electron beam lithography and its applications in the nanoelectronics industry. Another important application is the development and use of neutron scattering to study the nanostructures of inorganic, organic, and biomaterials. At present, there are numerous emerging nanotechnologies in which nuclear applications and radiation play decisive roles. These include nanoelectronics, biotechnology, diagnostics, and therapy. Based on present pioneering research programs, the future trends in nuclear applications in nanotechnology can be outlined as follows:

1. Neutrons: High flux reactors are excellent tools for exploring advanced neutron scattering. Neutron irradiation can also reveal insightful information about nano-structure multidimensional self-assembly and copolymers.[2,3]
2. Heavy charged particles (i.e. protons and alpha particles): The advancement of radiation oncology requires the application of nano-dosimetry, including measurements of the dose distribution within a single cancer cell.[4]
    - With a further understanding of radiation cell killing mechanisms in a mixed LET field, new nano-dosimetry based cell survival equations are being developed and benchmarked against experimental results. By introducing quantities on the nanometer scale, corresponding to DNA and chromatin-level lesions, a better model of the mechanisms of cell death and repair can be developed and instituted in radiology. [5]

3. Light charged particles and gamma radiolysis: Low linear energy transfer (LET) irradiation, as in the case of gamma radiolysis, electron beam irradiation (0.3-10 MeV), and positron irradiation will play major roles in synthesis, manufacturing, and material characterization in nanotechnology. This includes, but is not limited to the following:

    - Electron beam and gamma radiolysis manufacturing of nano composites.[6]
    - Electron beam and gamma radiolysis synthesis of nano gels for drug delivery systems, via intramolecular crosslinking of polymer chains.[7,8,9]
    - Electron beam and gamma radiation-induced grafting for bioengineering [10]
    - Electron beam radiation-induced synthesis of nano particles.
    - Positron irradiation for characterization of nano structures.

Electron beam irradiation provides a key tool for the development and investigation of a diverse range of nano and advanced technologies. Several examples of state-of-the-art research applications are described below:

A high-energy electron beam can be effectively used for sterilization and crosslinking of medical materials, such as ultra-high molecular weight polyethylene (UHMWPE). This polymer, used in total knee and hip replacements or arthroplasties, benefits from high-energy crosslinking in improved wear resistance. A high dose rate allows for bimolecular crosslinking between alkyl radicals generated through hydrogen abstraction, while minimizing oxidation from peroxyl radical formation. The medical polymer is simultaneously sterilized when irradiated over 25 kGy.

The curing of coatings, inks, and adhesives can also benefit from electron beam technology. This method eliminates hazardous air pollutants typically produced from conventional curing techniques, reduces the amount of energy consumed, and increases material performance and properties of the end use products. Acrylate, epoxide, and polyester systems are commonly used for applications such as food and flexible packaging, printing and graphic arts, wood varnishes, composites, adhesives, and pressure-sensitive adhesives.

Magnetic nanoparticle-organic polymer hybrid materials are an area of intense research interest due to their potential uses in a variety of applications, including magnetic data storage, medical diagnostic imaging, and drug delivery. However, in order for these materials to be useful, the dispersion of the particles which they contain must be controlled. One method of accomplishing this is through their placement within a polymer matrix which may undergo microphase separation to generate distinct hydrophilic regions into which they may be incorporated. Electron beam radiolytic preparation of a copolymer for use as the matrix has been investigated. Pulse radiolysis allows the study of fast kinetics and structure of radiation-induced ions and free radicals during synthesis.

Poly (N-isopropyl acrylamide) is an exceptional temperature responsive polymer which exhibits a hydrophobic/hydrophilic transition at 32°C. This unique property makes it a valuable material in the field of tissue engineering. A recent investigation showed that cultured cells grown on these temperature-responsive dishes can be harvested as intact sheets by controlling the temperature. This investigation involves the use of a high energy electron beam to covalently bond the polymer to the surface of culture dishes.[11]

Fuel cells are of great interest in the field of the generation of renewable energy currently under investigation. The small size of these devices, in addition to their high efficiency and low operating temperatures, allows them to be used as an effective portable energy source. One key element of the fuel cell is the polymer electrolyte membrane. Utilizing electron beams for radiation-induced grafting allows cost effective, customizable, and high quality preparation of such membranes.

Radiation-induced inter and intra-molecular crosslinking by an electron beam for the synthesis of nano-hydrogels is a new field with applications in drug and vaccine delivery. By varying the temperature of the polymers during irradiation, the hydrodynamic radius of the nano-hydrogel molecules can be customized via intra-crosslinking dominance. Encapsulation of a specific drug within this customizable hydrogel will allow site-specific delivery within biological systems.

High-energy electrons are also used in the environmental remediation of organic contaminants and polychlorinated biphenyls (PCBs). Toxic organic compounds in water are removed through oxidation, while reduction reactions dechlorinate PCBs in transformer oil and marine sediment. Pulse radiolysis studies reveal the mechanisms and kinetics of this remediation process.

In addition to these, electron beam applications involving electron induced defects in carbon nanotubes and nanotube structure transformation are also under investigation.

In this paper, we describe the differences in reaction mechanisms between high LET radiation, such as protons and alpha particles, and low LET radiation, such as 200 keV-10 MeV electrons and gamma irradiation.

Results and Discussion

1. High LET Irradiation (alpha particles, protons, heavy ions)

Despite their important applications in medicine and recent applications in nano technologies, protons, α^{2+}) particles and heavy ions in are not currently used in radiation processing. In addition to the prohibitive costs of the high LET radiation producing devices[1], the ranges of the high-Let particles in the materials are very short. For example, the range of 5.49 MeV α particles in H_2O is 0.0411 mm.

1.1 Interaction of α particles with H_2O and its applications in Boron Neutron Capture Therapy (BNCT)):

Little is known about the α radiolysis of substances in aqueous solutions. Radiolysis of H_2O with α produces a much smaller yield of OH radicals and than low- LET gamma radiolysis. While the yields obtained upon radiolysis with α particles with energy of about 5 MeV are G (OH) = 0.16 μmol J^{-1} and G) = < 0.02 μmol J^{-1}, the corresponding G-values obtained upon radiolysis of water with gamma rays or electrons with energies of 0.1 - 10 MeV are 0.29 μmol J^{-1} for both OH and .[12, 13, 14] Therefore, it should be expected that in the radiolysis of aqueous solutions by α particles, the extent of reducing effects by would be almost negligible, and the extent of the oxidizing effects of OH is much smaller than in the case of low LET radiolysis.

In BNCT (boron neutron capture therapy), the α particles are produced through the following reactions of thermal neutrons with drug containing ^{10}B molecules:

$$^{10}B + {}^{1}n \gamma {}^{7}Li^{+} (0.84 \text{ MeV}) + {}^{4}He^{2+} (1.47 \text{ MeV}) + \gamma (0.48 \text{ MeV}) \qquad 94\%$$

$$^{10}B + {}^{1}n \gamma {}^{7}Li (1.01 \text{ MeV}) + {}^{4}He^{2+} (1.78 \text{ MeV}) \qquad 6\%$$

$^{7}Li^{+}$ and $^{4}He^{2+}$ deposit their energies to the surroundings inside the cell within a 9μm range. The advantage of this very short range in comparison with the typical cell diameter is that $^{7}Li^{+}$ and $^{4}He^{2+}$ are theoretically capable of lethally attacking the ^{10}B containing cell components such as DNA and the RNA, while leaving neighboring cells unharmed [15,16]. The most important challenges of the BNCT technology reside in the enhancement of the selectivity of the BNCT drugs to make them suitable for pickup by the cancer cells while minimizing their uptake in surrounding normal (healthy) cells.[17,18]

1 It is not the intent of this article to discuss and compare the cost of irradiation producing devices

Figure 1, summary of the strategy of the use of BNCT in the treatment of a cancerous tumor in the prostate.

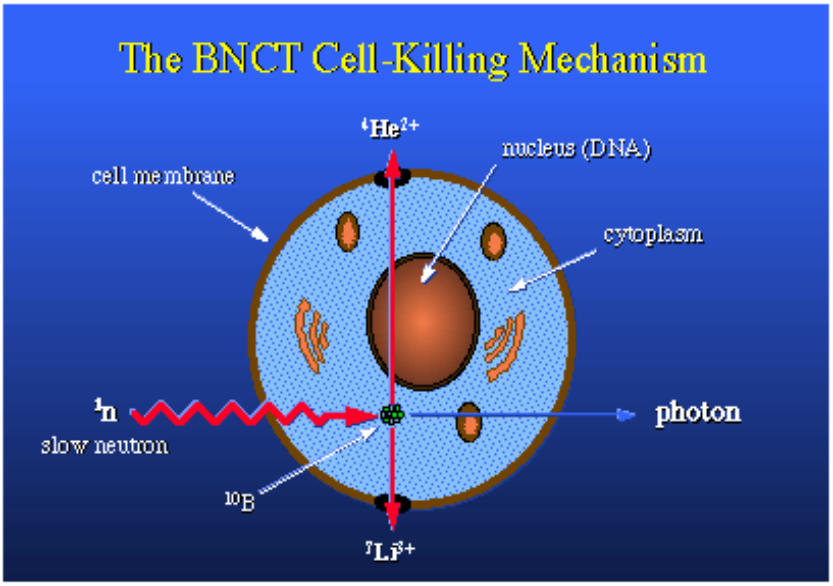

Figure 1: Low-energy neutrons interact with ^{10}B isotope to produce high-energy and short-range alpha particles and ^7Li. High LET alpha particles have a very short path length (<10mm). Neighboring cells will be unaffected. Particles release 200 keV/mm within the cell. Only a few particles are required to kill a cell. Cancerous tumor in the prostate can be targeted with a direct neutron beam due to its favorable location (away from vital organs).

Applications of High LET Charged Particles in Advanced Technology: Protons and Heavy Ions

Radiation-induced proton modifications of nanotubes

The synthesis of carbon-based ferromagnetic materials is one of the most challenging tasks in nano technologies. It has been reported that ferromagnetic properties can be generated upon irradiation of graphite with high-energy protons. [19,20,21] The success in producing ferromagnetic materials upon irradiation of graphite with protons raises the possibility of generating ferromagnetic properties in carbon nanotubes (CNTs). Attempts to functionalize the CNTs by proton irradiation have received wide attention because of the wide range of their applications. The composite of CNT with poly (3-octylthiophene) has recently been used for space photovoltaic applications.[22] To be qualified for space applications, studies of the radiation-induced damage by protons, electrons, heavy ions and cosmic gamma rays had to be performed on both CNT and poly (3-octylthiophene). The effects of proton irradiation on the interband transitions in single-wall carbon nanotubes in poly (3-octylthiophene) composite as a function of dose were studied in detail (Neupane et al).[23] This study showed that two interband transitions

could be observed at 0.71 and 1.28 eV upon radiolysis with 2 MeV protons at fluences ranging from 5 x 10^{10} cm^{-2} and 5.6 x 10^{15} cm^{-2}. This study also concluded that carbon nanotubes have excellent resistance to proton irradiation, and that the degradation of poly (3-octylthiophene) film is the limiting factor on determining the maximum fluence to which the composite can be exposed without excessive degradation.

Heavy Ion Irradiation

Unlike the low LET irradiation which can be used for synthesis and crosslinking of polymers, heavy ions irradiation mainly induces damage in materials. Despite these damage effects, heavy ions have increasingly used in the production of nanostructures for advanced technologies, such as nano porous materials.

Since many polymers have been used in satellites and spacecraft, where they are exposed to heavy ions irradiation, understanding of the degradation mechanisms and prediction of failures of these polymers caused by high LET have become essential. Heavy ions deposit their energies in amounts of the order of several keV per nanometer. This provides sufficient energy to cause massive scission of chemical bonds, leading to degradation of the polymers. This can be demonstrated in the difference between irradiating polyimides by low and high LET. Despite the fact that polyimides have high radiation resistance to low LET irradiation, it was demonstrated that polyimides undergo degradation when irradiated with 1.1 GeV Au ions.[24] Radiolytic gaseous products such as ethylene, carbon monoxide and nitrogen are the main degradation products which leave the polymer during the irradiation. In addition, carbon and acetylene are also formed. The proposed degradation mechanism is shown below.

The most commonly used ionizing radiations are electrons, γ-rays or X-rays. The energy is deposited randomly in the polymer substrate and the grafted domains are thus "homogeneously" distributed. Ionizing particles such as ions produced by Swift Heavy Irradiation (SHI) induce in the wake of their passing through the solid a continuous trail of excitations and ionizations leading to the formation of a latent track. The deposited energy is highly localized along the ion path and heterogeneous grafting occurs.

Ion track grafting in latent tracks was first performed by Monnin and Blanford in 1973 for nuclear tracks detection. [25] In the nineties, the team formed by Betz, Le Moel and Balanzat was the leader in ion track grafting in latent track for 15 years. [26,27] They have shown that the ion grafting is influenced by many parameters, including irradiation parameters, polymerization parameters and polymer substrate parameters. These parameters also affect the polydispersivity and the length of the grafted chains. Due to high electronic stopping power of the particles used in the grafting process, the grafting initiated by SHI (E> 1MeV.amu) is different from the one initiated with γ-rays. Moreover, the value of the grafting yield and the molecular weight distribution vary depending on the kind of ion used. Changing the substrate and/or the monomer leads to different structures of grafted films. They demonstrated that the grafting is localized in

the tracks at the earliest stages of the grafting due to faster diffusion rate of the monomer, and this rate is further increased by the grafting. When the grafting yield increases, the graft polymer spreads progressively around the latent track, destroying the crystalline structure in the bulk of the initial substrate, if this substrate is semi-crystalline, and progressively covering its surface. Due to diffusion factors of different origins, delocalization of the grafting outside the tracks appears to occur, leading to an increase in the dimensions of the polymer. Still, even at high grafting yields, SHI-induced grafting remains more heterogeneous than grafting by means of an electron beam or γ radiation. Application of ion track grafting was found in Polymer Electrolyte Membranes (PEMs) for fuel cells, where the production of proton conductive channels through a fluoropolymer significantly enhances the proton conductivity and diminishes the water uptake of the membrane during tests of the fuel cells. [28]

The latent tracks can be etched, and pores of different geometries can be obtained in a polymer depending on the ratio between the track etch rate and the bulk etch rate. For instance, cylindrical or biconical geometries may be produced.[29,30] These track-etched nanoporous membranes are commercially available for filtration applications (Whatman, Millipore). They are also used for template synthesis in academic studies aimed at growing metallic nanowires.[31] Such high aspect ratio nanowires have found applications in Spintronics, notably as Magnetic Random Access Memories (MRAM's) for information storage. Fundamental studies are under development, focused on both the shapes of the etched tracks and the properties of the polymers, such as electroactive polymers. [32] Formation of magnetic domain walls in magnetic nanowires has to be understood in order to take advantage of this phenomenon in creating new types of devices. Biconical tracks lead to constrictions in electrodeposited nanowires. [33] These constrictions are also under study with respect to their ability to trap domain walls or to create a tunneling effect. [34] Upon lowering the ion flux during SHI irradiation and cutting the beam at the right time, single track polymer membranes can be obtained. A single nanopore in a solid state polymer is of great interest nowadays for fundamental studies related to DNA sequencing or protein refolding, as well as conductivity properties. [35,36,37,38,39]

Cuscito and coworkers showed in 2007 that the polymerisation grafting initiated by residual radicals present in etched tracks of PVDF nanoporous membranes is localized inside the nanopores. [40] Other studies have extended this property to other polymers.[41] In this way, membranes with interesting properties related to the specific location of the chemical modifications are obtained. Some recent developments lead to production of sensors of water quality.[42] Reactive vinyl monomers are suitable for ion track grafting. However, when dealing with acrylate monomers, the grafted polymer chains have been observed to grow anarchically due to the large number of transfer reactions. This conventional method suffers from one simple flaw: the molecular weight and the polydispersity of the grafted chains cannot be controlled. To solve this problem and accurately tune the size of the nanopores, controlled radical polymerization, such as RAFT (reversible addition-fragmentation chain reaction) polymerization, has recently been successfully applied to these ion track membranes. [43]

Applications of low LET radiation (high energy photons, electrons, and positrons) in advanced technology

Characterization of nanostructures changes via positron annihilation lifetime spectroscopy

Unlike irradiation with electrons or gamma rays, irradiation with positrons has not been used in radiation processing and synthesis. Primarily, positron irradiation has been used for characterization of changes in nanostructures by means of annihilation spectroscopy. This technique is based on the annihilation reactions of the incoming positrons with electrons in the irradiated materials.

The mechanisms of interaction of low LET radiation with matter: Irradiation with gamma rays, x-rays, and electron beams

There is a very large body of literature concerning the use of low LET irradiation in the synthesis of nanostructures, polymerization and modification of polymers, grafting, environmental remediation, and radiation effects on materials, including sterilization and outer space applications, as well as synthesis of composites. In all cases, the mechanisms involve the early radiolytic productions of high yields of ions and free radicals which can initiate effective and productive reactions.

We have chosen as examples the following mechanisms for oxidative, reductive, or just neutral free radical reactions:

A. The photochemidtry of polyenyl radicals and its application to UHMWPE for use in artificial cartilages

Ultra-high molecular weight polyethylene (UHMWPE) has been the standard load-bearing material used in total joint replacements since the 1960s. However, oxidative degradation can lead to premature aging and wear of UHMWPE, requiring implant revision. We have been working on the following two methods to impede the degradation processes of the UHMWEP:

The UV-method:

The use of UV light as an alternative to thermal treatments above the melting point (150 °C) to remove free radicals in irradiated UHMWPE was explored. It was found that, in contrast with the allyl free radicals which are converted by 258-nm light to alkyl free radicals, polyenyl radicals are not converted to alkyl radicals by UV light. Nonetheless, by sandwiching UV light treatments between low temperature thermal anneals (100 °C), it was possible to reduce free radical concentrations by 30%. This reduction was achievable for depths of up to one millimeter. However, this reduction did not have a significant effect on oxidation due to an increase in oxidation susceptibility because of the concurrent increase in concentration of easily abstracted allylic hydrogens.

By photoirradiating for an optimal amount of time, it was possible, for the first time, to synthesize a polyethylene sample whose residual free radicals consisted almost entirely of dienyl free radicals. This allowed unambiguous identification and simulation of the EPR spectra of dienyl free radicals, showing these spectra to consist of a singlet containing nine peaks separated

by 9 G hyperfine separations. Figure 2 demonstrates the strategy of conversion the allyl radicals to alkyl radicals followed by thermal annealing.

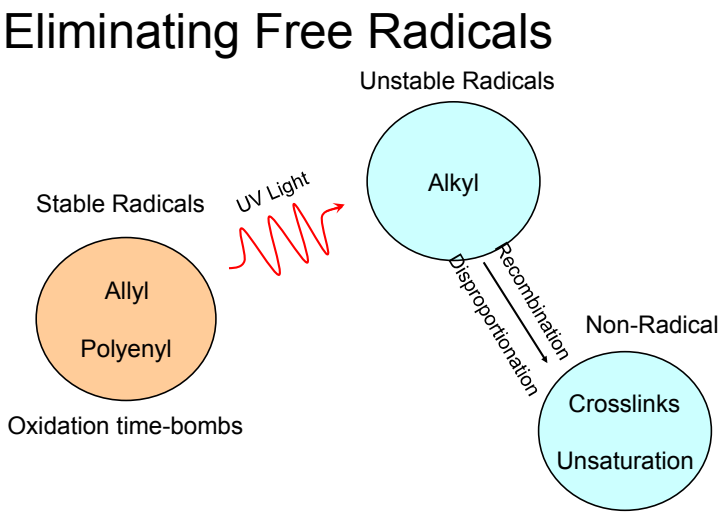

Figure 2: The photo-conversion of allyl to alkyl radicals followed by thermal annealing.

Detailed studies of photoirradiation of UHMWPE containing free radicals revealed that photoirradiation with a continuous spectrum above 200 nm causes the decay of diene unsaturations and allyl free radicals, a reduction in the overall amount of free radicals, and an increase in the degree of unsaturation of polyenyl free radicals. Upon exposure to photoirradiation over longer periods of time, polyenyl radicals were converted from lower to higher degrees of unsaturation. This effect was identical in the presence and in the absence of oxygen, but was suppressed by hydrogen gas. These results showed that the conversion does not occur through a mechanism of linear alkyl radical addition, wherein alkyl radicals migrate to stable polyene unsaturation sites and polyenyl radicals thereby increasing their order, as previously suggested. The valid mechanism appears to involve direct photoconversion of diene unsaturations to dienyl radicals and of lower order polyenyl radicals to higher order polyenyl.[44,45]

The radiation chemistry of polyethylene becomes more complicated in the presence of oxygen. Depending on the doserate and the oxygen concentrations, as well as the temperatures at which irradiation takes place, the radiolytically-produced free radicals can undergo various reactions. At high dose rate and in the absence or low concentrations of oxygen, crosslinking reactions are predominant. Figure 3 shows all the possible reactions of the free radicals in the absence as well as in the presence of oxygen.

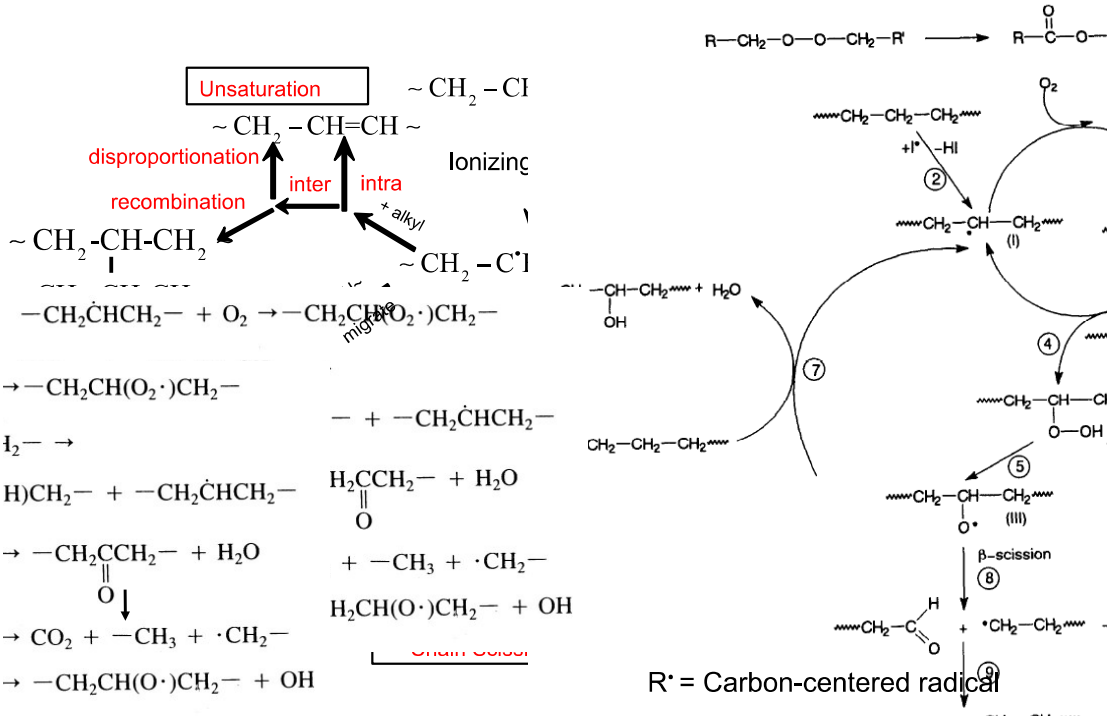

Figure 3: The mechanisms of the radiation chemistry of polyethylene in the presence and absence of oxygen

B. The radiolytic synthesis of nanogels for drug delivery systems

Studies of the radiation-induced synthesis of poly(vinylprrolidone) (PVP) nanogels, intended to provide a basis for obtaining intra-molecular cross-linked products, which are more useful in drug delivery, show that a sharp change in the controlling mechanism from inter-molecular to intra-molecular cross-linking occurs above a threshold temperature around 50 °C to 55 °C, even though the rate of inter-molecular cross-linking is enhanced as the temperature is raised. When aqueous solutions of PVP are irradiated, the activation energy of the decay of the PVP• radical is observed to rise sharply above this threshold temperature. This can be attributed to the collapse of the polymer chains, which occurs at temperatures above approximately 55 °C and leads to a reduction of the hydrolytic radius (R_h) of the irradiated polymer molecules at 77 °C to (44 ± 3) % of that of PVP molecules that were not irradiated at 20 °C, as shown by the results of asymmetric flow field flow fractionation (AFFFF) measurements. This accounts for the observation that the activation energy is higher within the temperature range above 55 °C. Higher pulse repetition rates during electron irradiation also promote intra-molecular cross-linking.

The mechanisms of the nanogel formation involve the formation of •PVP(-H) radicals through the abstraction of H atoms from the PVP by •OH radicals. Figure 4 illustrates the abstraction reactions of H atoms from the PVP molecule:

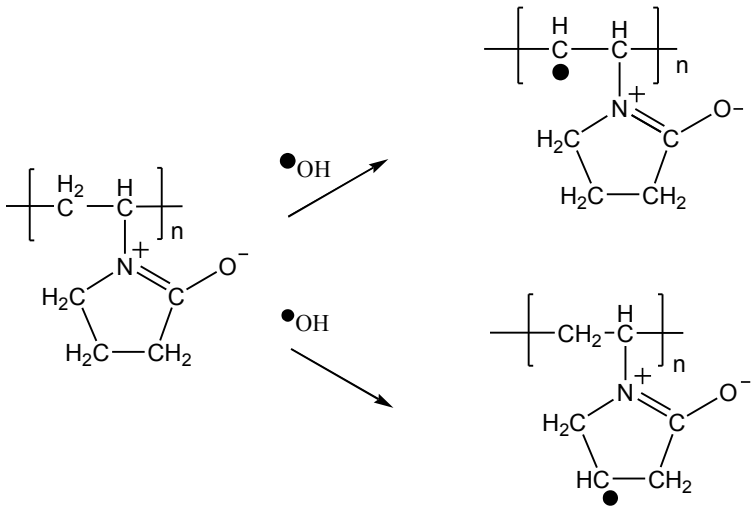

Figure 4: The abstraction reactions of H atoms by •OH radicals in the radiolysis of PVP aqueous solutions.

The formation of the •PVP(-H) radicals is followed by intra- and inter-crosslinking reactions. As shown in Figure 5, •PVP(-H) radicals can undergo either inter-crosslinking or intra-crosslinking reactions. To enhance the intra-crosslinking reaction, we have utilized high dose rates, high pulse repetition rates, and high temperatures.[46] Figure 5 shows the competition between the intra crosslinking reaction to produce the nano-gel on one hand and the inter-crosslinking reaction to produce macro-gel on the other in the radiolysis of PVP aqueous solutions.

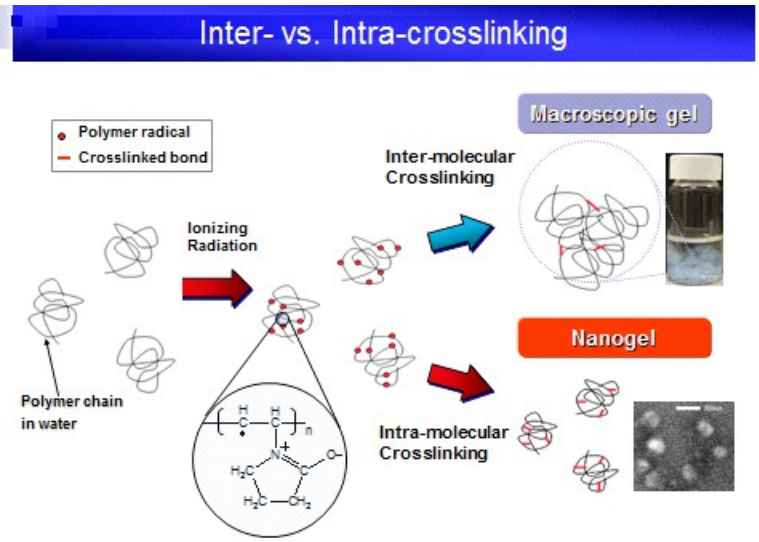

Figure 5 The competition between the intra-molecular crosslinking reaction to produce a nano gel, and the Inter-molecular crosslinking reaction to produce a macroscopic gel.

C. Extraction of Uranium from Seawater

It is well known that the amount of uranium resource in seawater is one thousand times of that in terrestrial ores. A polymeric adsorbent being capable of collecting uranium in seawater was developed in early 1980s in Japan with a limited capacity. These polymeric adsorbent fabrics have been synthesized by using ionizing radiation-induced graft polymerization to graft chelate function into numerous forms and shapes of polymers such as membranes, films, and fibers. Grafted adsorbentfunctionalities , in particular amidoxime (AO) have been successfully grafted by using ionizing radiation into polyethylene with various forms, in particular resins, fiber, membranes, and sheets. Actually, the polymer is grafted with acrylic moieties such as acrylonitrile and methacrylic acid, and the grfted polymer is subsequently reacted with hydroxylamine to produce the amidoxime-based adsorbrnt. It has been demonstrated that synthesis of adsorbents by means of radiation-induced grafting of amidoxime onto fibrous polyethylene produces an adsorbent which has a rate of adsorption of uranium and vanadium from seawater which is 100 times higher than that of commercialized resin. Yet, the low extraction efficiency and the lack of reusability due to degradation of polyethylene, have promoted advancing the research on developing new adsorbent fabrics that better meet the increasing demands on extraction of uranium from seawater.

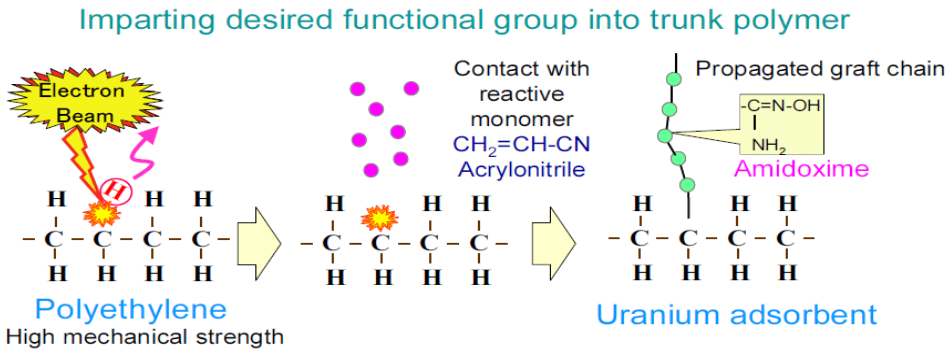

Figure 6: The synthesis of the absorbent fabric: The radiation-induced grafting of amidoxime on polyethylene

The uranium uptake from seawater obtained using the most current technologies, i.e. braids consisting of thin (e.g., 0.1-mm) polyethylene fibers radiation-grafted with amidoxime groups groups, is limited to no more than about 1.5 g U/kg adsorbent at 30 ºC and 1 g U/kg adsorbent at 20 ºC, even over contact periods of 40 days between the adsorbent and seawater. [47, 48,49] It has been observed that the adsorption capacity of amidoximated fibers for uranium is highest at pH values between pH 3-4 and 6, and is considerably lower (by a factor of approximately 3) at the pH of seawater around 8.2.[50] At this pH range, the major form of uranium(VI) is the anionic species $UO_2(CO_3)_3^{4-}$. However, the form being adsorbed on the amidoxime sites is the UO_2^{2+} cation, and decomplexation of $UO_2(CO_3)_3^{4-}$ into UO_2^{2+} is a rate-determining step in the sorption of U(VI) from seawater.[51] Accordingly, the use of complexing groups more efficient than amidoxime in reacting with uranium over a broader range (from 5-6 to 8.5), or of a combination of different adsorbing groups could result in higher capacities and adsorption rates.[52] Currently, further research is being performed by the authors' group and other groups, and it is aimed at developing novel types of polymeric adsorbent fabrics in order to obtain significantly enhancement of the capacity for extraction of the uranium from seawater, with high capacity for regeneration and reuse over many adsorption/desorption cycles.

D. Reductive remediation of PCBs

Widespread release of PCBs into the environment has presented a serious problem due to their persistence and toxicity. Ionizing radiation, such as gamma rays and high-energy electrons, is remarkably effective in dechlorinating PCBs to produce relatively benign biphenyls. The kinetics of the reductive dechlorination of PCBs in aqueous and aqueous micellar solutions and in transformer oil was studied by means of steady-state and pulse radiolysis methods. In aqueous micellar solutions, dichloro-, tetrachloro-, and decachlorobiphenyl congeners were solubilized in water using a commercially available non-ionic surfactant, Triton X-100. Electron pulse irradiation combined with time-resolved optical detection showed that the reaction rate constants of hydrated electrons $e_{aq}^{\bullet-}$ with decachlorobiphenyl and withTriton x-100in a 2 % Triton solution are 2.6 x 10^9 $Lmol^{-1}s^{-1}$ and 1.2 x 10^7 $Lmol^{-1}s^{-1}$, respectively. In addition, the reaction rate constant of $e_{aq}^{\bullet-}$ with dichlorobiphenyl in aqueous solutions has been determined to be 3.8 x 10^9 $Lmol^{-1}s^{-1}$. In aqueous propanol, the reaction rate constants of $e_{aq}^{\bullet-}$ with dichlorobiphenyl,

tetrachlorobiphenyl, and dechachlorobiphenyl are 2 x 10^9 $Lmol^{-1}s^{-1}$, 3 x 10^9 $Lmol^{-1}s^{-1}$, and 7 x 10^9 $Lmol^{-1}s^{-1}$, respectively. Figure 7 shows the electron capture reaction of the $e_{aq}^{\bullet-}$ and the addition reaction of the OH radicals to the phenyl group. Both reactions lead to dechlorination of the PCBs.

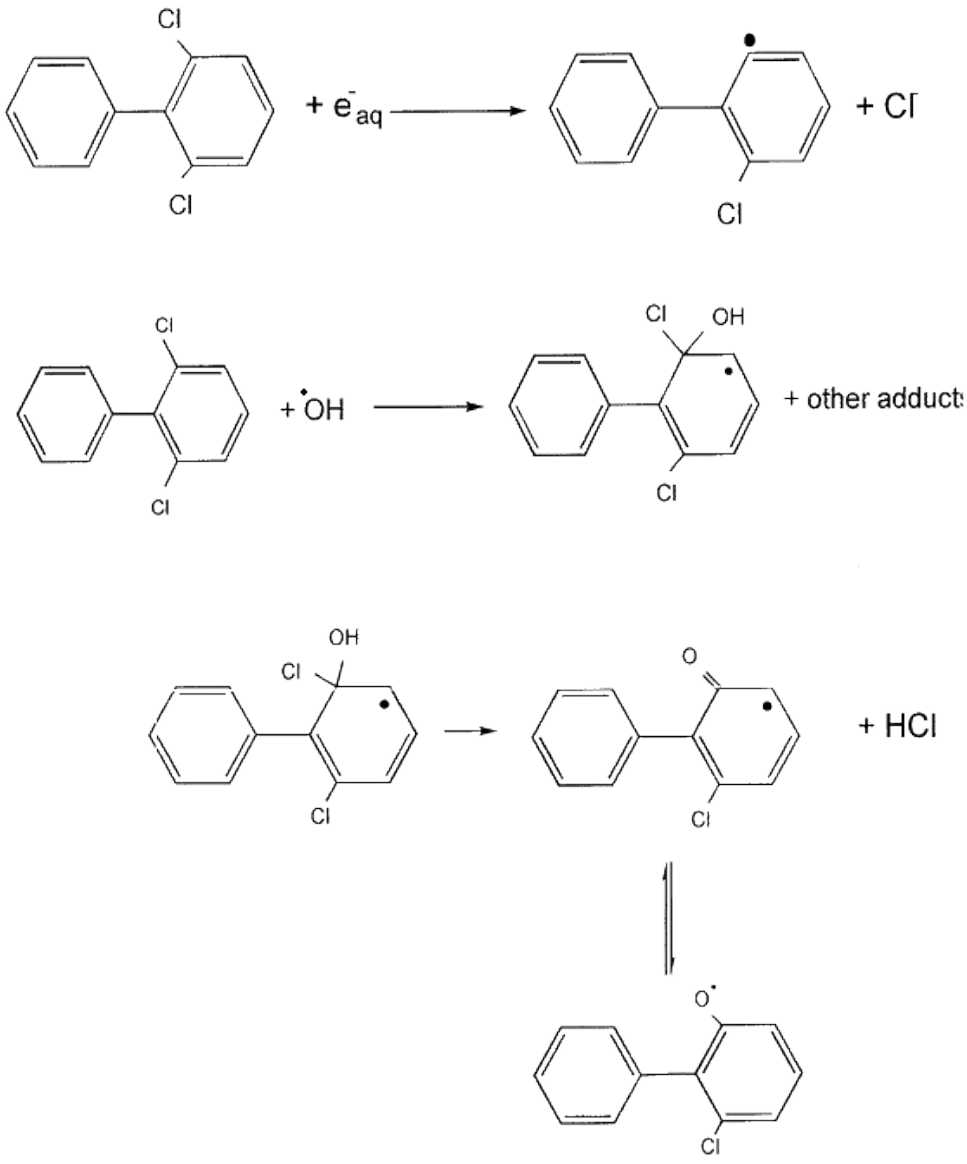

Figure 7: Dechlorination reactions of PCBs by $e_{aq}^{\bullet-}$ (reductive), and •OH radicals (oxidative)

In addition to PCBs as high-dielectric component, transformer oil contains many aromatic hydrocarbons, the most abundant being biphenyl, fluorene, and phenanthrene. Solvated electrons formed by irradiation of the oil react either with PCB to lead to dechlorination or with the aromatic hydrocarbons present in the oil to form radical anions. These species are shown to transfer an electron to chlorinated biphenyls relatively rapidly, leading to dechlorination. The rate constants for several such reactions, determined in 2-propanol solutions, are in the range of 10^7-10^8 $Lmol^{-1}s^{-1}$. These rapid reactions explain why PCB can be dechlorinated in oil despite the formation of biphenyl as radiolysis product that reacts rapidly with solvated electrons.[53,54]

A recent study by the authors shows that the oxidizing properties of ionizing radiation are of little value in the remediation of PCBs because of the high concentration of other organic species present. In contrast, the extreme effectiveness of radiation-induced reductive reactions for PCB remediation is not diminished by the presence of such contaminants.[55]

Conclusion

Although the interactions of high and low LET charged particles with matter are Columbic in nature, the short distances between the spurs in the high LET radiolysis have considerable impact on the primary yields of ions, excited molecules and atoms, and radicals. As the energies of the high LET particles increase, the distances between these spurs decrease, and eventually they will become connected to create large spurs with cylindrical shape. In these large spurs (or the cylindrical shape spurs) a competition will be established between the reactions of the primary ions, excited molecules and atoms with each other, and their diffusion to the medium outside the spurs. This explains the lower G(OH) in the radiolysis of aqueous solutions with high LET particles. Radiolysis with high LET enhances the reactions of OH radicals with themselves inside the spurs to produce H_2O_2. As a result, fewer OH radicals diffuse from the spurs to react with the solutes.

It should also be mentioned that despite the fact that the penetration and range of high LET particles are much shorter those of low LET particles, rendering them to be nonuseful for radiation processing and radiation synthesis, they have great advantages in radiation therapy. As shown in BNCT, ions, and proton therapy, the short range and penetration of these high LET particles increase their focus on the cancerous cells, and decrease their attack on the healthy ones. We see a very strong trend towards using high LET in radiation in oncology, and a corresponding departure from using low LET radiation such as electron beam and gamma.

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